Attention-Deficit/Hyperactivity Disorder (ADHD), characterised by developmentally inappropriate inattention, hyperactivity/impulsivity, or a combination of both, is a major public health problem. Neuroimaging studies have revealed associations of these cognitive impairments with structural and functional deficits all over the brain. Existing findings are not fully consistent due to the heterogeneity of study samples and diversity of research techniques. In the current study, we propose to utilise a multi-modal MRI approach to study the structural and functional brain networks in children with ADHD-combined type (ADHD-C) with a focus on the subgenual anterior cingulate cortex (sgACC). Diffusion tensor imaging (DTI) and resting-state functional MRI (rs-fMRI) data from 32 children with ADHD-C and 32 group-matched controls were involved. Network-based statistic (NBS) analysis of the rs-fMRI data revealed a disconnected functional network between the sgACC and multiple regions in the occipital lobe and cerebellum, whereas the DTI data showed disrupted white matter integrity in the subgenual cingulum bundle (sgCB). Post hoc Region-of-Interest (ROI)-based analyses showed significantly increased fluctuation of the spontaneous brain activity in the sgACC and higher radial diffusivity in the sgCB in the ADHD group. Both the rs-fMRI and DTI ROI-based measures were significantly correlated with clinical measures that examine behavioural capacities of attention and inhibitory control. Findings of this study suggest that functional alterations in the sgACC and white matter underdevelopment in the sgCB may impact each other, and together contribute to impaired attention and inhibitory control function in children with ADHD.